

PATENT SPECIFICATION

NO DRAWINGS

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International Classification:—C08f, C10m.

COMPLETE SPECIFICATION

Polymeric Materials

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

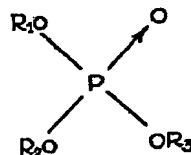
This invention relates to novel phosphorus containing polymeric compounds and more particularly to polymeric compounds useful as polyfunctional lubeoil additives that improve not only the load carrying capacity, but also one or more other properties, e.g. the viscosity/temperature characteristics and the detergency of lubricating oils, as well as to lubricating compositions containing such additives.

According to the present invention, novel copolymers comprise an alkenyl-substituted organo-phosphorus compound containing a phosphinyldyne group and at least one polymerisable mono-olefinically unsaturated compound having no phosphorus atoms in the molecule, at least one of the components of the copolymer having an oleophilic hydrocarbon chain of at least 8 carbon atoms.

Preferred copolymers are those in which the alkenyl phosphorus compound is a dialkenyl-substituted phosphorus compound containing a phosphinyldyne group and the mono-olefinically unsaturated compound has an oleophilic hydrocarbon chain of at least 8 carbon atoms. The term "phosphinyldyne group" is to be construed through the present

specification as meaning a $\equiv P \rightarrow O$ group, (cf. J.C.S. 1952, page 5125).

The alkenyl-substituted organo-phosphorus compounds containing a phosphinyldyne group may be derived from phosphoric acid, phosphonic acid, phosphinic acid or phosphine oxide. Thus a very suitable class of phosphorus compounds is that having the general formula:

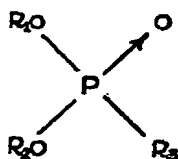


wherein at least one of the groups R_1 , R_2 and R_3 is an alkenyl or cycloalkenyl radical, and the other group(s) is(are) hydrogen, or an unsubstituted or substituted alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical. The alkenyl radical may be α : β -mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably are β : γ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CR^1_2-CR^1=CR^1_2$, where R^1 is a hydrogen atom or an alkyl group preferably having no more than 6 carbon atoms. The alkenyl radicals may be the same or different, but are preferably the same, if a di- or trialkenyl derivative is desired, and more preferably they are allyl radicals. Alkenyl esters of

phosphoric acid may be prepared by any method well-known in the art. For example the vinyl type esters may be prepared by dehydrohalogenation of compounds of the formula $(XCH_2CH_2O)_n(RO)_{3-n}P \rightarrow O$, where X is halogen, which compounds may be themselves prepared by reacting phosphorus/halogen compounds with ethylene oxide.

The allyl type esters can be prepared by reacting the desired phosphorus/halogen compound with a $\beta:\gamma$ mono-olefinically unsaturated alcohol in the presence of an acid-sequestant, e.g. pyridine. Examples of suitable phosphoric acid esters are allyl dihydrogen phosphate, dibutyl allyl phosphate, diethyl allyl phosphate, diallyl hydrogen phosphate, diallyl methyl phosphate, diallyl butyl phosphate, diallyl phenyl phosphate, diallyl cyclohexyl phosphate, allyl methallyl hydrogen phosphate, divinyl hydrogen phosphate, divinyl phenyl phosphate, bis(2-ethylallyl) hydrogen phosphate, dimethallyl benzyl phosphate, dicrotyl hydrogen phosphate, bis(2-pentenyl) hydrogen phosphate, bis(2-hexenyl) isopropyl phosphate and triallyl phosphate.

A further class of phosphorus compounds useful as monomers in the present invention is that having the general formula:

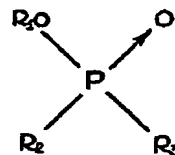


where at least one of the groups R_1 , R_2 and R_3 are alkenyl or cycloalkenyl groups and the other group(s) is (are) hydrogen, or an unsubstituted or substituted alkyl, cycloalkyl, aryl, alkaryl, or aralkyl radical. Preferably R_3 at least should be an alkenyl or cycloalkenyl radical. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α or β -alkyl substituted vinyl radicals, but preferably the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CH^1-CR^2=CR^3$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different but are preferably the same, if a di- or tri-alkenyl derivative is desired, more preferably they are allyl radicals. The above alkenyl derivatives of phosphoric acid may be prepared by any of the methods well-known in the art. For example, if R_1 and R_2 are both alkenyl radicals, the dialkenyl phosphonates may be conveniently prepared by reacting the desired phosphonic dihalide with the desired mono-olefinically unsaturated alcohol in the pre-

sence of an acid-sequestant, e.g. pyridine, to produce the diester. When R_2 and R_3 are alkenyl radicals, the desired compounds may be prepared by an Arbuzov reaction on a dialkyl alkenyl phosphite with an alkenyl halide. Where R_3 is the only alkenyl radical present, the required compound may be prepared by reacting phosphorus trichloride with an alkanol to produce a trialkyl phosphite which may then be reacted with an alkenyl halide to produce the required mono-alkenyl derivative.

Examples of suitable alkenyl derivatives of phosphonic acid are diethyl allylphosphonate, allyl butyl hydrogenphosphonate, allyl phenylphosphonic acid, diallyl phenylphosphonate, diallyl ethylphosphonate, diallyl butylphosphonate, divinyl ethylphosphonate, the mono-allyl ester of allylphosphonic acid, allyl methallyl phenylphosphonate, dicrotyl hydrogenphosphonate, diallyl benzylphosphonate, divinyl phenylphosphonate, di(2-pentenyl) ethylphosphonate, and diallyl allylphosphonate.

A further class of alkenyl phosphorus monomers that may be used in forming the copolymers of the present invention is that having the general formula:



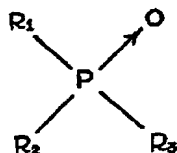
where at least one of the groups R_1 , R_2 and R_3 are alkenyl or cycloalkenyl and the other group(s) is (are) hydrogen or an unsubstituted or substituted alkyl, cycloalkyl, aryl, alkaryl or alkaryl radical. Preferably R_1 at least is an alkenyl or cycloalkenyl radical. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CH^1-CR^2=CR^3$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different but are preferably the same where a di- or trialkenyl derivative is desired, more preferably they are allyl radicals. The above alkenyl derivatives of phosphonic acid may be readily prepared by any of the methods known in the art.

If R_1 is alkenyl the $\beta:\gamma$ mono-olefinically unsaturated derivatives may be prepared by direct esterification of a phosphonic acid with the desired $\beta:\gamma$ mono-olefinically unsaturated alcohol. Alternatively, if R_1 is alkenyl and

a dialkenyl derivative is desired having both alkenyl radicals the same, a convenient method of preparation is to react a phosphonous dichloride with the desired $\beta:\gamma$ mono-olefinically unsaturated alcohol to form the diester of a phosphonous acid which undergoes an Arbuzov re-arrangement to form the ester of the corresponding phosphinic acid which may be separated from the reaction mixture by distillation.

If R_1 and R_2 are alkenyl radicals, the desired product may be obtained by reacting a dialkenyl phosphinous halide with a suitable alcohol or phenol in the presence of an acid sequestrant, e.g. dimethyl aniline. Examples of alkenyl derivatives of phosphinic acid are allyl phosphinate, the allyl ester of phenylethylphosphinic acid, the allyl ester of phenyl allyl phosphinic acid, the allyl ester of allyl phosphinic acid, the vinyl ester of vinylphenylphosphinic acid, diallyl phosphinic acid, allyl phenylphosphinic acid, allylmethylphosphinic acid, ethyl diallylphosphinate, phenyl divinylphosphinate, methyl allylmethylphosphinate and allyl diallylphosphinate.

A still further class of alkenyl phosphorus compounds useful in the present invention is that having the general formula:



where at least one of R_1 , R_2 and R_3 are alkenyl or cycloalkenyl radicals and the other group(s) is (are) hydrogen or an alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radical, which radicals may be optionally substituted. The alkenyl radicals may be $\alpha:\beta$ -mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CR^1_2-CR^1=CR^1_2$, where R^1 is a hydrogen atom or an alkyl preferably having up to six carbon atoms. The alkenyl radicals may be the same or different, but preferably they are the same if a di- or tri-alkenyl derivative is desired and more preferably they are allyl groups. Such phosphine oxides may readily be prepared by the reaction between a mono- or dihalophosphine or phosphorus trichloride and the desired alkenyl Grignard reagent followed by air oxidation. Alternatively, such compounds may be prepared by reacting a compound of the formula R_nRX_{3-n} , where R is aryl or alkyl or alkenyl and n is 1 or 2, with sulphur dioxide and chlorine to produce $R_nP(O)X_{3-n}$, and then reacting this product with an alkenyl Grignard reagent. Exemplary of suitable phosphine oxides are

allyl butyl phenyl phosphine oxide, diallyl *p*-methoxyphenyl phosphine oxide, diallyl phenyl phosphine oxide, diallyl *sec*-butyl phosphine oxide, divinyl phenyl phosphine oxide, diallyl butyl phosphine oxide, diallyl benzyl phosphine oxide, diallyl chloromethyl phosphine oxide, allyl methallyl phenyl phosphine oxide, dimethallyl phenyl phosphine oxide, dimethallyl isopropyl phosphine oxide and triallyl phosphine oxide.

Mixtures of two or more of the foregoing monomers can be used if desired. Where it is desired to include the oleophilic hydrocarbon chain of at least 8 carbon atoms in the phosphorus containing monomer, this can readily be done for example by a reacting compound having the formula $(RO)(A)P(O)H$ where A may be aryl, alkyl, alkoxy, aroxy or hydrogen, and R is alkyl or aryl, with an olefin having at least 8 carbon atoms, in the presence of a free radical initiator. The product can then be transesterified to replace the alkoxy or aroxy group(s) by alkenoxy group(s).

Typical of the polymerisable mono-olefinically unsaturated compounds with which the foregoing phosphorus compounds may be copolymerised are acrylic acid and α -substituted acrylic acids and their derivatives, such as their esters, nitriles and amides. Examples of such compounds are acrylic acid, methacrylic acid, ethacrylic acid, α -phenyl acrylic acid, the alkyl esters thereof, e.g. methyl ethyl, propyl, isopropyl, butyl, isobutyl, amyl, octyl, nonyl, lauryl, cetyl, oleyl, stearyl and cyclohexyl esters, acrylamide, α -methacrylamide, α -ethacrylamide, laurylacrylamide, acrylonitrile, α -methacrylonitrile, α -ethacrylonitrile, α -propylacrylonitrile, 2-butyl 2-hexenenitrile, 2-propyl 2-pentene-nitrile, 2-chloroethyl 2-butenenitrile, 2-ethyl 3-chloro 2-butenenitrile, 2-isopropyl 3-bromo 2-pentenenitrile, and α -isopropyl β -cyclohexyl-acrylonitrile.

Other compounds which may be copolymerised with the foregoing phosphorus compounds in the present invention are vinyl esters of organic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl laurate, vinyl stearate and vinyl benzoate, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl phenyl ether, vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, and phenyl vinyl ketone, vinyl aryl compounds such as styrene, ortho-methyl styrene, para-methyl styrene, para-ethyl styrene, α -methyl styrene and other alkyl derivatives of styrene in which the alkyl group or groups may be substituted in the ring or in the side chain or both, vinyl naphthalene and vinyl diphenyl, vinyl halides, e.g. vinyl chloride and vinyl fluoride and vinylidene halides, e.g. vinylidene chloride and vinylidene fluorochloride. Allyl esters, ethers and ketones corresponding to the vinyl compounds listed above may also be

used. Alpha, beta-unsaturated polycarboxylic acids and their derivatives such as maleic, fumaric, citraconic, itaconic and aconitic acids and their mono- and polyesters with aliphatic and aromatic alcohols, and their amides and nitriles, may also be used.

Other compounds which may be copolymerised with the foregoing phosphorus compounds in the present invention are the α -olefins particularly those having more than eight carbon atoms, amino-substituted olefins, e.g. *p*-(β -diethylaminoethyl)styrene and nitrogen-containing heterocyclic compounds having a mono-olefinically unsaturated substituent, e.g. the vinyl pyridines (whether 2-, 3- or 4-substituted) and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 4-methyl-2-vinyl pyridine, 4-ethyl-2-vinyl pyridine and 2-butyl-5-vinyl pyridine. Vinyl lactams are also suitable monomers, particularly the *N*-vinyl pyrrolidones or *N*-vinyl piperidones. The vinyl radical may be mono-alkyl substituted.

It is preferable that the monomers copolymerised with the phosphorus containing monomers according to the present invention, contain an oleophilic hydrocarbon chain of at least eight carbon atoms and which is preferably an alkyl radical of 12 to 20 carbon atoms. It will be appreciated that mixtures of the above monomers may be used in forming the copolymers according to the present invention. Particularly preferred copolymers are those formed from alkenyl-substituted organo-phosphorus compounds with a higher alkyl ester of acrylic or methacrylic acid, i.e. where the ester group contains 8 or more carbon atoms, e.g. lauryl methacrylate. Minor proportions of lower alkyl esters of acrylic or methacrylic acids, e.g. methyl methacrylate, may additionally be present in such copolymers.

The molar ratio of phosphorus-containing monomer to the polymerisable comonomer may vary between wide limits and generally lies between 20:1 and 1:20. Preferably the ratio lies between 5:1 and 1:10, with ratios between 3:1 to 1:10 being especially suitable.

The copolymers of the invention can be prepared by any suitable means. Normally the reactants are copolymerised in the presence of a catalyst. Oxygen-yielding catalysts, such as organic peroxides, may be used. These may be aliphatic, aromatic, heterocyclic, or alicyclic peroxides, such as diethyl peroxide, tertiary butyl hydroperoxide, di(tertiary butyl) peroxide, benzoyl peroxide, dimethyl thienyl peroxide, dilauroyl peroxide and urea peroxide. Other catalysts include sodium bisulphite, diethyl sulphoxide, ammonium persulphate, alkali metal perborates and azo compounds, e.g. azo-(bis-isobutyro) nitrile. The catalysts are generally used in an amount

of 0.1 to 5% by weight of the reactants.

The copolymerisation reaction may be carried out under a variety of conditions. For example, the reaction can be carried out in the presence or absence of an inert solvent, such as a hydrocarbon, under a blanket of nitrogen or carbon dioxide and at a temperature varying from room temperature or lower to about 180°C or higher for a period of from about 2 to 48 hours. In general the preferred copolymers have a molecular weight in the range 50,000—400,000.

The following examples illustrate the production of copolymers of the present invention.

EXAMPLE I

A solution of 277 g. of allyl alcohol 326 g. pyridine and 280 ml of ether was cooled to approximately -30°C by means of a bath of iso-propyl alcohol (I.P.A.)/Cardice (the word Cardice is a registered trade mark) and was then added to a solution of 255 g. phosphorus oxychloride in 132 ml. ether over a period of two hours. After the first hour a further 100 ml. of ether was added to facilitate stirring. The reaction mixture was stirred for a further three hours after which time the pyridinium chloride formed was filtered off. The filtrate was evaporated leaving triallylphosphate as a clear yellow oil.

51 g. of the triallylphosphate was dissolved in 100 mls. of I.M.S. and refluxed with 100 mls of 5N aqueous solution hydroxide for two hours. The solvents were then removed under pressure (100°C/15 mm) and the residual oil was extracted with ether in order to remove unhydrolysed phosphate. The oil was then treated with dilute hydrochloric acid until acid and the oil thus separated was extracted with ether to produce diallyl hydrogen phosphate.

A mixture of 3.4 g. of the diallyl hydrogen phosphate and 25 g. of lauryl methacrylate in 15.5 g. of technical white oil and 20 ml. of benzene was treated with 0.5 g. benzoyl peroxide and treated at 70°C. for 18 hours with stirring. The benzene was then evaporated to leave the copolymer in a solution of white oil. The molecular ratio of the diallyl hydrogen phosphate to lauryl methacrylate in the copolymer was 1:6.

EXAMPLE II

Phenylphosphonous dichloride was prepared by refluxing together 525 mls phosphorus trichloride, 468 mls benzene and 300 g. of aluminium chloride for four hours. Phosphorus oxychloride (223 mls) was then added and the mixture briefly refluxed. Excess benzene and phosphorus trichloride was evaporated under vacuum and the residue cooled to about 40°C and extracted with ligroin. From the extract, crude phenylphosphonous dichloride was recovered and purified by redistillation under reduced pressure.

5 A solution of 60.5 g. of allyl bromide in 285 ether was added dropwise to 12 g. magnesium in 100 mls ether. After stirring for 1 hour, 23 g. of phenylphosphonous dichloride in 100 mls of ether was added and the mixture stirred overnight. A solution of 50 g. of ammonium chloride in 250 mls. water was added and the ethereal layer was separated, dried over sodium sulphate and evaporated.

10 The resultant crude diallylphenylphosphine was purified by redistillation. All these operations were conducted in a nitrogen atmosphere.

15 5.5 g. of the diallylphenyl phosphine was dissolved in 12 mls of benzene and air passed through the solution for thirty minutes to produce diallyl phenyl phosphine oxide. To this solution was added 23 ml. benzene, 20 15 g. of technical white oil, 7 g. of lauryl methacrylate and 0.5 g. of benzoylperoxide. The mixture was heated to 75°C. and stirred for 24 hours. At the end of each of the first three hours, 25 a further amount of 7 g. lauryl methacrylate was added and with the third addition, a further 0.5 g. of benzoyl peroxide was added. The benzene was evaporated at reduced pressure and the residue heated at 100°C/1 mm Hg for 30 minutes. The resulting copolymer 30 solution of diallyl phenyl phosphine oxide and lauryl methacrylate in technical white oil was soluble in mineral oil. The molecular ratio of diallyl phenyl phosphine oxide to lauryl methacrylate was 1:4.

EXAMPLE III

35 Phenyl phosphonous dichloride (prepared as in Example II, 90 g) was dissolved in carbon tetrachloride (500 ml) and the whole cooled to -50°C by a cardice/IPA coolant. Dry chlorine gas was now bubbled into the solution until the exothermic reaction was complete. The product was filtered whilst 40 cool to give a residue of phenyl phosphonic tetrachloride. Further quantities of this material was obtained by evaporation of the mother liquors. The product was purified by recrystallation from carbon tetrachloride, followed by drying in a vacuum desiccator.

50 Phenyl phosphonic tetrachloride (63 g) was dissolved in benzene (250 ml) and the stirred mixture treated with sulphur dioxide until reaction was complete. The reaction is rapid and the phenyl phosphonic dichloride 55 $\text{Ph} \cdot \text{POCl}_2$ produced was recovered by distillation b.p. 87°C/1mm. Hg. Phenyl phosphonic dichloride (49 g) was added slowly with stirring to a solution of allyl alcohol (29 g) and pyridine (40 g) in ether (250 ml) cooled to 0°C. The rate of addition was such that the temperature of the mixture remained at 0°C. Stirring was continued for 2 hours after complete addition. The reaction product was filtered to remove pyridine hydrochloride 65 and the residue washed with 200 ml. ether.

The ether was evaporated from the filtrate and the residue distilled to give diallyl phenyl phosphonate b.p. 112°C/0.3 mm Hg.

To the solution of diallyl phenyl phosphonate (5.9 g.) and lauryl methacrylate (25.4 g.) in mineral oil (15.5 g) at 140°C, 70 ditert-butyl peroxide (0.4 ml) was added and the whole stirred vigorously. The solution was maintained under these conditions for 5 hours. The product had a molar ratio of 1:4 diallyl phenyl phosphonate to lauryl methacrylate and was a 66.7% concentrate in mineral oil. This concentrate was readily soluble in further samples of mineral oil. 75

EXAMPLE IV

80 To a solution of allyl alcohol (135 g) and pyridine (168 g) in diethyl ether (2000 ml), phenyl phosphonous dichloride was added slowly with stirring. The rate of addition was adjusted to maintain a gentle reflux. Stirring and refluxing were continued for a further two hours after complete addition. Pyridine hydrochloride was filtered off and the residue washed with more ether (500 ml). The ether was evaporated from the filtrate and the product distilled, the bulk of the material (allyl phenyl allylphosphinate) boiling at 102°C/0.4 mms. Hg. Small amounts of diallyl phenylphosphonate are separated during the distillation b.p. 79°C/0.4 mms. Hg. 95

To a solution of allyl phenyl allylphosphinate (6 g) and lauryl methacrylate (28 g) in mineral oil (68 g) at 140—5°C di-tert-butyl peroxide (0.4 ml) was added and the whole stirred vigorously for 24 hours. The product was heated at 100°C/0.5 mm. Hg. for 30 minutes but no distillate was obtained. This product has a 1:4 molar ratio of allyl phenyl allylphosphinate to lauryl methacrylate and was a 33.3% concentrate in mineral oil. 100

EXAMPLE V

110 151.2 gm of phosphorus trichloride was added to a solution of 151.8 gm of ethanol and 269 gm of pyridine in 151.8 gm of a petroleum ether boiling at 60—80°C, over a period of two hours. The temperature was maintained at 0—5°C by a cardice/IPA cooling bath. The reaction mixture was stirred for a further hour after complete addition, during this time the mixture was allowed to warm to room temperature. The product was filtered to remove pyridine hydrochloride and the solvent and phosphorus trichloride were then stripped from the filtrate. The residue was distilled to give triethyl phosphite. 115

120 121 gm of allyl bromide containing a small quantity of hydroquinone was refluxed in a 500 ml. flask under a 10 inch column packed with glass beads, 140 gms of triethylphosphite was added starting at a rate which maintained a steady reflux. Material boiling at 37—39°C was run off from a Weir head at the top of the column. After 8 hours, no more low 130

boiling material remained and the reaction mixture was distilled to produce diethyl allylphosphonate.

- 5 133.5 gms of diethyl allylphosphonate, 190.5 gms lauryl methacrylate, 445 gms of a SAE 10W30 grade mineral oil and 7.5 gms of di-tert-butyl peroxide were mixed and stirred together at 145°C. After ½ hour a further quantity of 190.5 gms laurylmethacrylate was added, this was repeated after 2 hours and again after 4 hours. The product was then stirred for a further 90 minutes. The mixture was then stripped at 140° C and 0.15 mm Hg pressure and a residue consisting of a 66.6% concentrate of a copolymer of diethyl allylphosphonate and lauryl methacrylate in a molar ratio of 1:8 in the mineral oil was recovered.

EXAMPLE VI

- 20 557 gms of allyl alcohol, 724 gms of pyridine and 500 mls of sodium dried toluene were stirred at 0—5°C. 413 gms of phosphorus trichloride in 100 mls of sodium dried toluene was then added whilst maintaining the temperature of 0—5°C. The product was stirred for ½ hour and then the amine hydrochloride was filtered off. The toluene was then stripped off leaving triallyl phosphite.

- 30 448 gms of n-butyl bromide containing a small amount of hydroquinone was heated to reflux in a vessel fitted with a column packed with glass beads surmounted by a Weir head. 220 gms of triallyl phosphite was added and refluxing continued for 20 hours and material boiling below 97°C was removed. Excess butyl bromide was then distilled off and the residue comprised diallyl butylphosphonate. 109 gms of diallyl butylphosphonate, 508 gms of lauryl methacrylate, 927 gms of an SAE 10W30 grade mineral oil and 7.6 gms of di-tert-butyl peroxide were heated at 145°C for 4 hours. The final product was a 40% wt. concentrate in the oil of a copolymer of diallyl butylphosphonate and lauryl methacrylate having a monomer ratio of 1:4.

EXAMPLE VII

- 50 127 g of the triallyl phosphate prepared as in Example I, lauryl methacrylate (191 g.) and benzoyl peroxide (7 g.) in dry benzene (200 ml.) were stirred for 1 hour at 75°C. Lauryl methacrylate (400 g.) was added to the stirred mixture over 7 hours and stirring continued for 16 hours after completing the addition. The temperature remained at 75°—78° throughout. Most of the solvent was removed under reduced pressure and the viscous residue poured with vigorous stirring, into methanol (2000 ml.). The precipitated copolymer was washed with methanol by decanting and stripped of solvent under reduced pressure to yield a clear oil soluble copolymer (575 g.) of triallyl phosphate and

lauryl methacrylate. Phosphorous content of copolymer: 1.08%, Ratio of monomers 1:4.

The copolymers of the present invention are particularly useful as additives in lubricating compositions, and such compositions are a further feature of the present invention.

The lubricating oil to which the copolymers may be added to provide lubricating compositions of the invention can be any natural or synthetic oil having lubricating properties. Thus, the oil can be a hydrocarbon lubricating oil obtained from paraffinic or naphthenic crude or mixtures thereof. The viscosity of these oils may vary over a wide range, such as from 100 SUS to 100°F to 100 SUS at 210°F. The hydrocarbon lubricating oil may be blended with fatty oils such as castor oil or lard oil, and/or with synthetic lubricating oils such as polymerised olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e.g. di(2-ethyl hexyl)sebacate, dioctyl phthalate and trioctyl phosphate and polyalkyl silicone polymers such as dimethyl silicone polymers. If desired, the synthetic lubricating oils may be used as the sole base lubricating oil or admixed with fatty oils or derivatives thereof.

In the lubricating compositions of the present invention the polymeric additive is present in a minor proportion by weight based on the total composition, generally from 0.01% to 20% and preferably from 0.1% to 8% by weight.

It will be understood that the lubricating compositions of the invention may be modified by the addition thereto of minor proportions of other additives such as methacrylate polymers, metal dithiophosphates, e.g. zinc di-2-ethylhexyl dithiophosphate, metal organic sulphonates, e.g. neutral or basic calcium, barium or zinc petroleum sulphonate; metal thiocarbamates, e.g. zinc, chromium or calcium dibutyl or diamyl dithiocarbamate; amines, e.g. phenyl-alpha-naphthylamine or octadecylamine; alkylated phenols and alkylated bisphenols, e.g. 2,6-ditertiary-butyl-4-methylphenol and 4,4'-methylene bis(2,6-ditertiarybutyl phenol); organic sulphides, e.g. dibenzyldisulphide.

Lubricating compositions of the present invention are useful as engine oils, gear oils, turbine oils and in various other fields of lubrication where good detergency, viscosity/temperature characteristics and load carrying properties are essential.

Compositions of this invention are illustrated by the following formulations; the ratios in brackets being the mole ratios of the monomers used for preparing the copolymers. The mineral lubricating oil used in an oil having a viscosity of 10 cs at 210°F.

COMPOSITION A

Copolymer of diallyl hydrogen phosphate/lauryl methacrylate (1 : 6)	4% wt.
Mineral Oil	balance

COMPOSITION B

Copolymer of diallyl hydrogen phosphate/lauryl methacrylate (1 : 8)	4% wt.
Mineral oil	balance

COMPOSITION C

Copolymer of diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	3.5% wt.
Mineral oil	balance

COMPOSITION D

Copolymer of the allyl ester of phenyl-allyl phosphinic acid/lauryl methacrylate (1 : 4)	2.0% wt.
4,4'-methylene-bis(2,6-di-tert. butyl phenol)	0.75% wt.
Mineral oil	balance

COMPOSITION E

Copolymer of diallyl phenyl phosphonate/lauryl methacrylate (1 : 4)	6.8 wt. %
Mineral oil	balance

COMPOSITION F

Copolymer of diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	3.9% wt.
4,4'-methylene-bis(2,6-ditertiarybutyl phenol)	0.75% wt.
Mineral oil	balance

COMPOSITION G

Copolymer of diethyl allyl phosphonate/lauryl methacrylate (1 : 8)	2% wt.
4,4'-methylene-bis(2,6-ditert. butyl phenol)	0.75% wt.
Mineral oil	balance

COMPOSITION H

Copolymer of diallyl butylphosphonate/lauryl methacrylate (1 : 4)	2% wt.
4,4'-methylene-bis(2,6-ditert. butyl phenol)	0.75 %wt.
Mineral oil	balance

COMPOSITION I

Copolymer of triallyl phosphate/lauryl methacrylate (1 : 4)	2% wt.
4,4'-methylene-bis(2,6-ditert. butyl phenol)	0.75% wt.
Mineral oil	balance

5 In order to illustrate the properties of lubricating compositions and the utility of copolymers according to the present invention, certain compositions were subjected to tests in the following manner.

The thickening ability of the copolymers used as additives in the present invention was assessed in terms of the VT coefficient, calculated from the formula:

10

$$VT = \frac{\frac{\eta_{\text{blend}}^{210^\circ \text{ F.}}}{\eta_{\text{base oil}}^{210^\circ \text{ F.}}} - \frac{\eta_{\text{blend}}^{100^\circ \text{ F.}}}{\eta_{\text{base oil}}^{100^\circ \text{ F.}}}}{\frac{\eta_{\text{blend}}^{210^\circ \text{ F.}}}{\eta_{\text{base oil}}^{210^\circ \text{ F.}}} - \frac{\eta_{\text{blend}}^{100^\circ \text{ F.}}}{\eta_{\text{base oil}}^{100^\circ \text{ F.}}}} \times 100$$

where η is the viscosity.

Various copolymers were added to a base mineral lubricating oil having a viscosity of 10 cS at 210°F and the VT values deter-

mined from the above equation. The results 15 are contained in Table I.

TABLE I

Copolymer	Concentration	VT
Diallyl hydrogen phosphate/lauryl methacrylate (1 : 6)	4% wt.	109
Allyl ester of phenyl allyl phosphinic acid/lauryl methacrylate (1 : 4)	4.1% wt.	117
Diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	2% wt.	109

These figures represent good thickening properties.

20 The dispersant properties of various compositions were illustrated in the following manner.

25 1 part by weight of used straight mineral oil from a diesel engine and containing about 2% w of oil-insolubles was mixed with 5 parts of the unused mineral oil of Compositions A—I. In this blend the insoluble particles were clustered. Other blends were made containing, as before, 1/6th of used

oil, and the remaining 5/6th a series of increasing concentrations of one of the additives in the unused mineral oil. At a particular concentration the insoluble particles become dispersed, and this concentration is taken as a measure of the dispersancy of the additive, i.e. the lower the concentration, the better are the dispersancy characteristics. 30
35 Some results are given in Table II.

TABLE II

Copolymer	Concn. of copolymer required to disperse clusters in mg per g blend
Diallyl phosphate/lauryl methacrylate (1 : 6)	0.4
Diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	0.3
Diethyl allylphosphonate/lauryl methacrylate (1 : 4)	0.8
Triallyl phosphate/lauryl methacrylate (1 : 4)	1.7
Diethyl allylphosphonate /lauryl methacrylate (1 : 8)	0.67
Diallyl phenylphosphonate/lauryl methacrylate (1 : 4)	1.0
Dibutyl allyl phosphine oxide/lauryl methacrylate (1 : 4)	0.4
A mixture of diallyl butylphosphonate and diallyl phosphate in 9 : 1 molar ratio/lauryl methacrylate (1 : 4)	0.67
A mixture of diallyl butylphosphonate and diallyl phosphate in 4:1 molar ratio/lauryl methacrylate (1 : 4)	0.67

Compositions D, F, G, H and I exhibited good low temperature performance properties when used in an automotive engine as is evidenced by absence of sludge deposition in the sump. Further, Compositions F and H were submitted to an anti-scuffing test in an automotive engine in which the cam wear and degree of tappet scuffing is indicative of the load carrying capacity of the oil. Compared with a similar formulation, but in which the copolymer according to the invention is replaced by 4% wt. of a copolymer of lauryl-methacrylate and vinyl pyrrolidone, Composition F exhibits a 60% reduction in the amount of tappet scuffing and an 83° reduction in cam wear and Composition H exhibits a 50% reduction in the amount of tappet scuffing and a 90% reduction in cam wear. Also, Compositions A and D, when subjected to a test for extreme pressure properties on the 4-ball machine, exhibited 2½ second seizure delay loads of 137 kg and 92 kg respectively compared with 65 kg for the base oil.

WHAT WE CLAIM IS:—

1. A copolymer comprising an alkenyl-substituted organo-phosphorus compound containing a phosphinylidene group and at least one polymerisable mono-olefinically unsaturated compound having no phosphorus atoms in the molecule, at least one of the

components of the copolymer having an oleophilic hydrocarbon chain of at least 8 carbon atoms.

2. A copolymer as claimed in claim 1, wherein the phosphorus compound has the formula $(R_1O)(R_2O)(R_3O)P \rightarrow O$; wherein at least one of the groups R_1 , R_2 and R_3 is an alkenyl or cycloalkenyl radical and the other group(s) is (are) hydrogen or an unsubstituted or substituted alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical.

3. A copolymer as claimed in claim 1, wherein the phosphorus compound has the formula $(R_1O)(R_2O)(R_3)P \rightarrow O$; wherein at least one of the groups R_1 , R_2 and R_3 is an alkenyl or cycloalkenyl radical and the other group(s) is (are) hydrogen or an unsubstituted or substituted alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical.

4. A copolymer as claimed in claim 1, wherein the phosphorus compound has the formula $(R_1O)(R_2)(R_3)P \rightarrow O$; wherein at least one of the groups R_1 , R_2 and R_3 is an alkenyl or cycloalkenyl radical and the other group(s) is (are) hydrogen or an unsubstituted or substituted alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical.

5. A copolymer as claimed in claim 1, wherein the phosphorus compound has the formula $(R_1)(R_2)(R_3)P \rightarrow O$; wherein at

- least one of the groups R_1 , R_2 and R_3 is an alkenyl or cycloalkenyl radical and the other group(s) is (are) hydrogen or an unsubstituted or substituted alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical.
6. A copolymer as claimed in any one of the preceding claims, in which the alkenyl radicals are $\alpha:\beta$ -mono-olefinically unsaturated hydrocarbon radicals.
7. A copolymer as claimed in any one of claims 1 to 5, wherein the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-\text{CR}^1_2-\text{CR}^1=\text{CR}^2_2$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms.
8. A copolymer as claimed in claim 7, in which the alkenyl radicals are allyl radicals.
9. A copolymer as claimed in any one of the preceding claims, in which the phosphorus compound is a di-alkenyl-substituted compound.
10. A copolymer as claimed in any one of the preceding claims, wherein the polymerisable mono-olefinically unsaturated compound having no phosphorus in the molecule is an acrylic acid or an ester, nitrile or amide thereof.
11. A copolymer as claimed in claim 10, wherein said unsaturated compound is an alkyl ester of acrylic or methacrylic acid wherein the ester group contains 8 or more carbon atoms.
12. A copolymer as claimed in claim 11, wherein the ester is lauryl methacrylate.
13. A copolymer as claimed in claim 11 containing additionally a minor proportion of a lower alkyl ester of acrylic or methacrylic acid.
14. A copolymer as claimed in any one of the preceding claims, wherein the molar ratio of phosphorus-containing monomer to the polymerisable comonomer lies between 20:1 and 1:20.
15. A copolymer as claimed in claim 14, wherein said molar ratio lies between 5:1 and 1:10.
16. A copolymer comprising diallyl hydrogen phosphate and lauryl methacrylate in a molar ratio of between 20:1 and 1:20.
17. A copolymer comprising diallyl butylphosphonate and lauryl methacrylate in a molar ratio of between 20:1 and 1:20.
18. A copolymer comprising diallyl phenyl phosphine oxide and lauryl methacrylate in a molar ratio of between 20:1 to 1:20.
19. Novel copolymers substantially as hereinbefore described with special reference to the examples.
20. A lubricating composition comprising a lubricating oil and a minor proportion by weight of a copolymer claimed in any one of claims 1 to 19.
21. A lubricating composition as claimed in claim 20 comprising additionally minor proportions by weight based on the lubricating oil of other additives.
22. A lubricating composition as claimed in claim 21, wherein the additional additive is an amine, alkylated phenol or alkylated bisphenol.
23. A lubricating composition substantially as hereinbefore described with special reference to Compositions A to I.

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PROVISIONAL SPECIFICATION

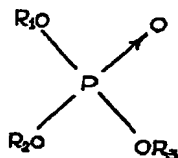
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Lubricating Compositions and Additives therefor

- We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare this invention to be described in the following statement:—
- This invention relates to lubricating compositions containing ashless polymeric additives, particularly additives that improve the load carrying capacity of lubricating oils, and more particularly polyfunctional additives that improve not only the load carrying capacity, but also one or more other properties, e.g. the viscosity/temperature characteristics and the detergency of lubricating oils.
- According to the present invention, lubricating compositions comprise a major proportion of a lubricating oil and a minor proportion of a copolymer of a dialkenyl substituted phosphorus compound containing a phosphinylidyne group and at least one polymerisable mono-olefinically unsaturated compound. Preferred monomers to be copolymerised with the phosphorus compounds are mono-olefinically unsaturated compounds having an oleophilic hydrocarbon chain of at least 8 carbon atoms.
- A further feature of the present invention is the provision of novel oil-soluble copolymers comprising a dialkenyl substituted phosphorus compound containing a phosphinylidyne group and at least one polymerisable mono-olefinically unsaturated compound having an oleophilic hydrocarbon chain of at least 8 carbon atoms. The term "phosphinylidyne group" is to be construed throughout the present specification as mean-

ing a $\equiv P \rightarrow O$ group, (cf. J.C.S. 1952 page 5125).

The dialkenyl substituted phosphorus compounds containing a phosphinylidene group may be derived from phosphoric acid, phosphonic acid, phosphinic acid or phosphine oxide. Thus a very suitable class of phosphorus compounds is that having the general formula:



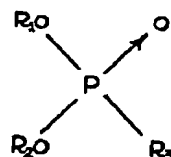
where R_1 and R_2 are alkenyl or cycloalkenyl radicals and R_3 is a hydrogen atom, or an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical. R_1 and R_2 may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably R_1 and R_2 are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-\text{CR}^1_2-\text{CR}^1=\text{CR}^1_2$, where R^1 is a hydrogen atom or an alkyl group preferably having no more than 6 carbon atoms. R_1 and R_2 may be the same or different, but are preferably the same, and more preferably they are allyl radicals. Dialkenyl esters of phosphoric acid may be prepared by any method well-known in the art. For example the vinyl type esters may be prepared by dihydrohalogenation of compounds of the formula



where X is halogen, which compounds may be themselves prepared by reacting phosphorus chlorides with ethylene oxide.

The allyl type esters can be prepared by reacting the desired phosphorodichloridate with a $\beta:\gamma$ mono-olefinically unsaturated alcohol in the presence of an acid-sequestant, e.g. pyridine. Examples of suitable phosphoric acid esters are diallyl hydrogen phosphate, diallyl methyl phosphate, diallyl phenyl phosphate, diallyl cyclohexyl phosphate, allyl methallyl hydrogen phosphate, divinyl hydrogen phosphate, divinyl phenyl phosphate, bis(2-ethylallyl) hydrogen phosphate, dimethallyl benzyl phosphate, dicrotyl hydrogen phosphate, bis(2-pentenyl) hydrogen phosphate and bis(2-hexenyl) isopropyl phosphate.

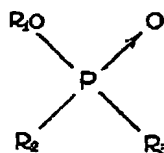
A further class of phosphorus compounds useful as monomers in the present invention is that having the general formula:



where any two of the groups R_1 , R_2 and R_3 are alkenyl or cycloalkenyl groups and the other group is hydrogen, alkyl, cycloalkyl, aryl, alkaryl, or aralkyl. Preferably R_1 and R_2 are alkenyl or cycloalkenyl radicals. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α or β -alkyl substituted vinyl radicals, but preferably the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-\text{CR}^1_2-\text{CR}^1=\text{CR}^1_2$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different but are preferably the same, more preferably they are allyl radicals. The above dialkenyl derivatives of phosphonic acid may be prepared by any of the methods well-known in the art. For example if R_1 and R_2 are alkenyl radicals, the dialkenyl phosphonates may be conveniently prepared by reacting the desired phosphonic dihalide with the desired mono-olefinically unsaturated alcohol in the presence of an acid-sequestant, e.g. pyridine to produce the diester. When R_2 and R_3 are dialkenyl radicals, the desired compounds may be prepared by an Arbuzov reaction on a dialkyl alkenyl phosphite with an alkenyl halide.

Examples of suitable dialkenyl derivatives of phosphonic acid are diallyl phenylphosphonate, diallyl ethylphosphonate, divinyl ethylphosphonate, the mono-allyl ester of allylphosphonic acid, allyl methallyl phenylphosphonate, dicrotyl phosphonate, diallyl benzylphosphonate, divinyl phenylphosphonate and di(2-pentenyl) ethylphosphonate.

A further class of dialkenyl phosphorus monomers that may be used in forming the copolymers of the present invention is that having the general formula



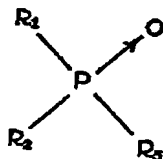
where two of the groups R_1 , R_2 and R_3 are

alkenyl or cycloalkenyl and the other group is hydrogen, alkyl, cycloalkyl, aryl, aralkyl or alkaryl. Preferably R_1 is an alkenyl or cycloalkenyl radical. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-\text{CR}^1_2-\text{CR}^1=\text{CR}^1_2$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different but are preferably the same, more preferably they are allyl radicals. The above dialkenyl derivatives of phosphonic acid may be readily prepared by any of the methods known in the art.

If R_1 is alkenyl the $\beta:\gamma$ mono-olefinically unsaturated derivatives may be prepared by direct esterification of an alkenyl phosphonic acid with the desired $\beta:\gamma$ mono-olefinically unsaturated alcohol. Alternatively if R_1 is alkenyl and both alkenyl radicals in the product are to be the same, a convenient method of preparation is to react a phosphorous dichloride with the desired $\beta:\gamma$ mono-olefinically unsaturated alcohol to form the diester of a phosphinous acid which partially undergoes an Arbusov re-arrangement to form the ester of the corresponding phosphinic acid which may be separated from the reaction mixture by distillation.

If R_2 and R_3 are both alkenyl radicals, the desired product may be obtained by reacting a phosphorodihalidate of the formula $\text{RO P}(\text{O})\text{X}_2$ with an alkenyl Grignard reagent, e.g. R^1MgBr (R^1 is alkenyl) to form $\text{RO P}(\text{O})\text{R}^1$. Examples of dialkenyl derivatives of phosphinic acid are the allyl ester of phenyl-prop-2-enyl-phosphinic acid, the allyl ester of prop-2-enyl phosphinic acid, the vinyl ester of vinylphenylphosphinic acid, diallyl phosphinic acid, allylmethylphosphinic acid, ethyl diallylphosphinate, phenyl divinylphosphinate and methyl allylmethylphosphinate.

A still further class of dialkenyl phosphorus compounds useful in the present invention is that having the general formula:



where R_1 and R_2 are alkenyl or cycloalkenyl radicals and R_3 is a hydrogen atom or an alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radical. R_1 and R_2 may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g.

vinyl or α - or β -alkyl substituted vinyl radicals, but preferably R_1 and R_2 are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-\text{CR}^1_2-\text{CR}^1=\text{CR}^1_2$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. R_1 and R_2 may be the same or different, but preferably they are the same and more preferably they are allyl groups. Such phosphine oxides may readily be prepared by the reaction between a dihalophosphine and the desired alkenyl Grignard reagent followed by air oxidation. Exemplary of suitable phosphine oxides are diallyl phenyl phosphine oxide, divinyl phenyl phosphine oxide, diallyl ethyl phosphine oxide, diallyl benzyl phosphine oxide, allyl methylallyl phenyl phosphine oxide, dimethylallyl phenyl phosphine oxide and dimethylallyl isopropyl phosphine oxide.

Mixtures of two or more of the foregoing monomers can be used if desired.

Typical of the other polymerisable mono-olefinically unsaturated compounds with which the foregoing phosphorus compounds may be copolymerised are acrylic acid and α -substituted acrylic acids and their derivatives, such as their esters, nitriles and amides. Examples of such compounds are acrylic acid, methacrylic acid, ethacrylic acid, α -phenyl acrylic acid, the alkyl esters thereof, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, octyl, nonyl, lauryl, cetyl, oleyl, stearyl and cyclohexyl esters, acrylamide, α -methacrylamide, α -ethacrylamide, laurylacrylamide, acrylonitrile, α -methacrylonitrile, α -ethacrylonitrile, α -propylacrylonitrile, 2-butyl 2-hexenenitrile, 2-propyl 2-pentenitrile, 2-chloroethyl 2-butenitrile, 2-ethyl 3-chloro 2-butenitrile, 2-isopropyl 3-bromo 2-pentenitrile, and α -isopropyl β -cyclohexyl-acrylonitrile.

Other compounds which may be used to form the copolymers used in the present invention are vinyl esters of organic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl cinnamate and vinyl crotonate, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl phenyl ether, vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, and phenyl vinyl ketone, vinyl aryl compounds such as styrene, ortho-methyl styrene, para-methyl styrene, para-ethyl styrene, α -methyl styrene and other alkyl derivatives of styrene in which the alkyl group or groups may be substituted in the ring or in the side chain or both, vinyl naphthalene and vinyl diphenyl, vinyl halides, e.g. vinyl chloride and vinyl fluoride and vinylidene halides, e.g. vinylidene chloride and vinylidene fluorochloride. Allyl esters, ethers and ketones corresponding to the vinyl compounds listed above may also be used.

Alpha, beta-, unsaturated polycarboxylic acids and their derivatives such as maleic, fumaric, citraconic, itaconic, crotonic, aconitic and tricarballic acids and their mono- and polyesters with aliphatic and aromatic alcohols, and their amides and nitriles, may also be used.

Other compounds which may be used to form the phosphorus containing copolymers used in the present invention are the α -olefins particularly those having more than eight carbon atoms, amino-substituted olefins, e.g. *p*-(β -diethylaminoethyl)styrene and nitrogen-containing heterocyclic compounds having a mono-olefinically unsaturated substituent, e.g. the vinyl pyridines (whether 2-, 3- or 4-substituted) and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 4-methyl-2-vinyl pyridine, 4-ethyl-2-vinyl pyridine and 2-butyl-5-vinyl pyridine. Vinyl lactams are also suitable monomers, particularly the *N*-vinyl pyrrolidones or *N*-vinyl piperidones. The vinyl radical may be mono-alkyl substituted.

Of the above listed monomers copolymerisable with the phosphorus containing monomers according to the present invention, it is preferred that they contain an oleophilic hydrocarbon chain of at least eight carbon atoms which is preferably an alkyl radical of 12 to 20 carbon atoms, and such copolymers per se are a feature of the present invention. It will be appreciated that mixtures of the above monomers may be used in forming the copolymers used as lubricating oil additives according to the present invention. Particularly preferred copolymers are those formed from dialkenyl substituted phosphorus compounds with a higher alkyl ester of an acrylic or methacrylic acid, i.e. where the ester group contains 8 or more carbon atoms, e.g. lauryl methacrylate. Minor proportions of lower alkyl esters of acrylic or methacrylic acids, e.g. methyl methacrylate, may advantageously be present in such copolymers.

The molar ratio of phosphorus containing monomer to the polymerisable comonomer may vary between wide limits and generally lies between 20:1 and 1:20. Preferably the ratio lies between 1:1 and 1:20, with ratios between 1:3 and 1:10 being especially suitable.

The copolymers of this invention can be prepared by any suitable means. Normally the reactants are copolymerised in the presence of a catalyst. Oxygen-yielding catalysts, such as organic peroxides, may be used. These may be aliphatic, aromatic, heterocyclic, or alicyclic peroxides, such as diethyl peroxide, tertiary butyl hydroperoxide, di(tertiary butyl) peroxide, benzoyl peroxide, dimethyl thienyl peroxide, dilauroyl peroxide and urea peroxide. Other catalysts include

sodium disulphite, diethyl sulphoxide, ammonium persulphate, alkali metal perborates and azo compounds, e.g. azo-(bis-isobutyro)nitrile. The catalysts are generally used in an amount of 0.1 to 5% by weight of the reactants.

The copolymerisation reaction may be carried out under a variety of conditions. For example, the reaction can be carried out in the presence or absence of an inert solvent, such as a hydrocarbon, under a blanket of nitrogen or carbon dioxide and at a temperature varying from room temperature or lower to about 180°C. or higher for a period of from about 2 to 48 hours.

It is preferred that the reaction be carried out in such a way that the resulting copolymer has a molecular weight above 50,000 and preferably between 75,000 and 1,000,000.

The following examples illustrate methods of producing copolymers of the present invention.

EXAMPLE 1

A solution of 277 g. of allyl alcohol and 326 g. of pyridine in 280 ml of ether was cooled to approximately -30°C. by means of a bath of iso-propyl alcohol (I.P.A.)/Cardice (the word Cardice is a registered trade mark) and was then added to a solution of 255 g. phosphorus oxychloride in 132 ml. ether over a period of two hours. After the first hour a further 100 ml. of ether was added to facilitate stirring. The reaction mixture was stirred for a further three hours after which time the pyridinium chloride formed was filtered off. The filtrate was evaporated leaving triallylphosphate as a clear yellow oil.

51 g. of the triallylphosphate was dissolved in 100 mls. of I.M.S. and refluxed with 100 mls. of 5N aqueous solution hydroxide for two hours. The solvents were then removed under reduced pressure (100°C/15 mm) and the residual oil was extracted with ether in order to remove unhydrolysed phosphate. The oil was then treated with dilute hydrochloric acid until acid and the oil thus separated was extracted with ether to produce diallyl hydrogen phosphate.

A mixture of 3.4 g. of the diallyl hydrogen phosphate and 25 g. of lauryl methacrylate in 15.5 g. of technical white oil and 20 ml. of benzene was treated with 0.5 g. benzoyl peroxide and treated at 70°C. for 18 hours with stirring. The benzene was then evaporated to leave the copolymer as a viscous, oil-soluble product. The molar ratio of the diallyl hydrogen phosphate to lauryl methacrylate in the copolymer was 1:6.

EXAMPLE 2

Phenylphosphonous dichloride was prepared by refluxing together 525 mls. phosphorous trichloride, 468 mls. benzene and 300 g. of aluminium chloride for four hours. Phosphorous oxychloride (223 mls.) was then added

and the mixture briefly refluxed. Excess benzene and phosphorus trichloride was evaporated under vacuum and the residue cooled to about 40°C. and extracted with ligroin. From the extract, crude phenphosphonous dichloride was recovered and purified by redistillation under reduced pressure.

5 A solution of 60.5 g. of allyl bromide in 285 mls ether was added dropwise to 12 g. magnesium in 100 mls ether. After stirring for 1 hour, 23 g. of phenylphosphonous dichloride in 100 mls of ether was added and the mixture stirred overnight. A solution of 50 g. of aluminium chloride in 250 mls water was added and the ethereal layer was separated, dried over sodium sulphate and evaporated.

10 The resultant crude diallylphenylphosphine was purified by redistillation. All these operations were conducted in a nitrogen atmosphere.

5.5 g. of the diallylphenyl phosphine was dissolved in 12 mls of benzene and air passed through the solution for thirty minutes to produce diallyl phenyl phosphine oxide. To this solution was added 23 ml. benzene, 15 g. of technical white oil, 7 g. of lauryl methacrylate and 0.5 g. of benzoylperoxide. The mixture was heated to 75°C. and stirred for 24 hours. At the end of each of the first three hours, a further amount of 7 g. lauryl methacrylate was added and with the third addition, a further 0.5 g. of benzoyl peroxide was added. The benzene was evaporated at reduced pressure and the residue heated at 100°C/1 mm Hg for 30 minutes. The resulting copolymer solution of diallyl phenyl phosphine oxide and lauryl methacrylate in technical white oil was soluble in mineral oil. The molar ratio of diallyl phenyl phosphine oxide to lauryl methacrylate was 1:4.

EXAMPLE 3

Phenyl phosphonous dichloride (prepared as in Example 2, 90 g) was dissolved in carbon tetrachloride (500 ml) and the whole cooled to -50 °C. by a cardice/IPA coolant. Dry chlorine gas was bubbled into the solution until the exothermic reaction was complete. The product was filtered whilst cool to give a residue of phenyl phosphonic tetrachloride. Further quantities of this material was obtained by evaporation of the mother liquors. The product was purified by recrystallisation from carbon tetrachloride, followed by drying in a vacuum desiccator.

55 Phenyl phosphonic tetrachloride (63 g) was dissolved in benzene (250 ml) and the stirred mixture treated with sulphur dioxide until reaction was complete. The reaction is rapid and the phenyl phosphonic dichloride Ph.POCl_2 produced was recovered by distillation b.p. 87°C/1 mm. Hg. Phenyl phosphonic dichloride (49 g) was added slowly with stirring to a solution of allyl alcohol 65 (29 g) and pyridine (40 g) in ether (250 ml)

cooled to 0°C. The rate of addition was such that the temperature of the mixture remained at 0°C. Stirring was continued for 2 hours after complete addition. The reaction product was filtered to remove pyridine hydrochloride and the residue washed with 200 ml ether. The ether was evaporated from the filtrate and the residue distilled to give diallyl phenyl phosphonate b.p. 112°C/0.3 mm Hg.

To a solution of diallyl phenyl phosphonate (5.9 g) and lauryl methacrylate (25.4 g) in mineral oil (15.5 g) at 140°C, di-tert-butyl peroxide (0.4 ml) was added and the whole stirred vigorously. The solution was maintained under these conditions for 5 hours. The product had a molar ratio of 1:4 diallyl phenyl phosphonate to lauryl methacrylate and was a 66.7% concentrate in mineral oil. This concentrate was readily soluble in further samples of mineral oil.

EXAMPLE 4

To a solution of allyl alcohol (135 g) and pyridine (168 g) in diethyl ether (2000 ml), phenyl phosphonous dichloride was added slowly with stirring. The rate of addition was adjusted to maintain a gentle reflux. Stirring and refluxing were continued for a further two hours after complete addition. Pyridine hydrochloride was filtered off and the residue washed with more ether (500 ml). The ether was evaporated from the filtrate and the product distilled, the bulk of the material (allyl phenyl - prop - 2 - enyl - phosphinate) boiling at 102°C/0.4 mms. Hg. Small amounts of diallyl phenyl phosphonite are separated during the distillation b.p. 79°C/0.4 mms. Hg.

To a solution of allyl phenyl prop-2-enyl phosphinate (6 g) and lauryl methacrylate (28 g) in mineral oil (68 g) at 140-5°C di-tert butyl peroxide (0.4 ml) was added and the whole stirred vigorously for 24 hours. The product was heated at 100°C/0.5 mm. Hg. for 30 minutes but no distillate was obtained. This product had a 1:4 molar ratio of allyl phenyl prop-2-enyl phosphinate to lauryl methacrylate and was a 33.3% concentrate in mineral oil.

Other copolymers useful in lubricating compositions of this invention include those listed below.

Diallyl phenyl phosphate/acrylamide, diallyl cyclohexylphosphate/vinyl laurate, dimethallyl hydrogen phosphate/lauryl methacrylate, diallyl phenyl phosphonate/vinyl laurate, divinyl ethylphosphonate/acrylonitrile, dimethallyl ethylphosphonate/oleyl maleate, allyl prop-2-enylphosphonate/lauryl methacrylate, diallyl phosphinic acid/stearyl methacrylate, divinyl phenyl phosphine oxide/acrylonitrile, dimethallyl phenyl phosphine oxide/2-methyl-5-vinyl pyridine and diallyl ethylphosphine oxide/lauryl methacrylate.

The lubricating oil in the lubricating compositions of the invention can be any natural or synthetic oil having lubricating properties. Thus, the oil can be a hydrocarbon lubricating oil obtained from paraffinic or naphthenic crude or mixtures thereof. The viscosity of these oils may vary over a wide range, such as from 100 SUS at 100°F to 100 SUS at 210°F. The hydrocarbon lubricating oil may be blended with fatty oils such as castor oil or lard oil, and/or with synthetic lubricating oils such as polymerised olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e.g. di(2-ethyl hexyl)sebacate, dioctyl phthalate and tri-octyl phosphate and polyalkyl silicone polymers such as dimethyl silicone polymers. If desired, the synthetic lubricating oils may be used as the sole base lubricating oil or admixed with fatty oils or derivatives thereof.

In the lubricating compositions of the present invention the polymeric additive is present in a minor proportion by weight based on the total composition, generally from 0.01% to 20% and preferably from 0.1% to 8% by weight.

It will be understood that the lubricating compositions of the invention may be modified by the addition thereto of minor proportions of other additives such as metal dithiophosphates, e.g. zinc di-2-ethylhexyl dithiophosphate, metal organic sulphomates, e.g. neutral or basic calcium, barium or zinc petroleum sulphonate; metal thiocarbonates, e.g. zinc, chromium or calcium dibutyl or diamyl dithiocarbamate; amines, e.g. phenyl-alpha-naphthylamine or octadecylamine; alkylated phenols and alkylated bisphenols, e.g. 2,6-ditertiarybutyl-4-methylphenol and 4,4'-methylene bis (2,6-ditertiarybutyl phenol); organic sulphides, e.g. dibenzyldisulphide.

Lubricating compositions of the present invention are useful as engine oil, gear oils, turbine oils and various other fields of lubrication where detergency, viscosity index and load carrying properties are essential.

Compositions of this invention are illustrated by the following formulations; the ratios in brackets being the mole ratios of the monomers used for preparing the copolymers. The mineral lubricating oil used is an oil having a viscosity of 10 cs at 210°F.

COMPOSITION A

Copolymer of diallyl hydrogen phosphate/lauryl methacrylate (1 : 6)	4% wt.
Mineral oil	balance

COMPOSITION B

Copolymer of diallyl hydrogen phosphate/lauryl methacrylate (1 : 8)	4% wt.
Mineral oil	balance

COMPOSITION C

Copolymer of diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	3.5% wt.
Mineral oil	balance

COMPOSITION D

Copolymer of the allyl ester of phenyl-prop-2-enyl phosphonic acid/lauryl methacrylate (1 : 4)	2.7% wt.
Mineral oil	balance

COMPOSITION E

Copolymer diallyl phenyl phosphonate/lauryl methacrylate (1 : 4)	6.8% wt.
Mineral oil	balance

COMPOSITION F

Copolymer of diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	3.9% wt.
4,4'-methylene-bis(2,6'-ditertiarybutyl phenol)	0.75% wt.
Mineral oil	balance

In order to illustrate the properties of lubricating compositions according to the present invention, certain compositions were subjected to tests in the following manner.

The thickening ability of the copolymers used as additives in the present invention was assessed in terms of the VT coefficient, calculated from the formula:

$$VT = \frac{\frac{\eta_{\text{blend}}^{210^\circ \text{ F.}}}{\eta_{\text{base oil}}^{210^\circ \text{ F.}}} - \frac{\eta_{\text{blend}}^{100^\circ \text{ F.}}}{\eta_{\text{base oil}}^{100^\circ \text{ F.}}}}{\frac{\eta_{\text{blend}}^{210^\circ \text{ F.}}}{\eta_{\text{base oil}}^{210^\circ \text{ F.}}} - \frac{\eta_{\text{blend}}^{100^\circ \text{ F.}}}{\eta_{\text{base oil}}^{100^\circ \text{ F.}}}} \times 100$$

where η is the viscosity.

Various copolymers were added to a base mineral lubricating oil having a viscosity of 10 c.s. at 210°F. and the VT values deter-

mined from the above equation. The results are contained in Table I.

TABLE I

Copolymer	Concentration	VT
Diallyl hydrogen phosphate/lauryl methacrylate (1 : 6)	4% wt.	109
Allyl ester of phenyl-prop-2-enyl-phosphinic acid/lauryl methacrylate (1 : 4)	4.1% wt.	117
Diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	2% wt.	109

These figures represent good thickening properties. The dispersant properties of various compositions were illustrated in the following manner.

1 part by weight of used straight mineral oil containing about 2%w of oil-insolubles, from a diesel engine was mixed with 5 parts of the unused mineral oil of Composition A—F. In this blend the insoluble particles

are clustered. Other blends are made containing, as before, 1/6th of used oil, and the remaining 5/6th a series of increasing concentrations of one of the additives in the unused mineral oil. At a particular concentration the insoluble particles become dispersed, and this concentration is taken as a measure of the dispersancy of the additive. Some results are given in Table 2.

TABLE II

Copolymer	Concn. of copolymer required to disperse clusters in mg per g blend
Diallylphosphate/lauryl methacrylate (1 : 6)	0.4
Diallylphenylphosphine oxide/lauryl methacrylate (1 : 4)	0.3

Composition F exhibited good low temperature performance properties when used in an automotive engine as is evidenced by absence of sludge deposition in the sump. Further, composition F was submitted to an anti-scuffing test in an automotive engine in which the cam wear and degree of tappet scuffing is indicative of the load carrying capacity of the oil. Compared with a similar formulation, but in which the 3.9% of the copolymer according to the invention is replaced by 4% wt. of a copolymer of lauryl-methacrylate and vinyl pyrrolidone, composition

F exhibits a 60% reduction in the amount of tappet scuffing and 90% reduction in cam wear. Also, compositions A and D, when subjected to a test for extreme pressure properties on the 4-ball machine, exhibited $2\frac{1}{2}$ second seizure delay loads of 137 kg and 92 kg. respectively compared with 65 kg for the base oil.

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PROVISIONAL SPECIFICATION

No. 36950 A.D. 1960

Polymeric Materials

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3, do hereby declare this invention to be described in the following statement:—

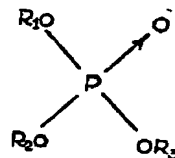
This invention relates to novel phosphorus containing polymeric compounds and more particularly to polymeric compounds useful as poly-functional luboil additives that improve not only the load carrying capacity, but also one or more other properties, e.g. the viscosity/temperature characteristics and the detergency of lubricating oils, as well as to lubricating compositions containing such additives.

According to the present invention, novel copolymers are derived from an alkenyl substituted phosphorus compound containing a phosphinylidene group and at least one polymerisable mono-olefinically unsaturated compound, at least one of the components of the copolymer having an oleophilic hydrocarbon chain of at least 8 carbon atoms.

Preferred copolymers are those in which the alkenyl phosphorus compound is a dialkenyl substituted phosphorus compound containing a phosphinylidene group and the mono-olefinically unsaturated compound has an oleophilic hydrocarbon chain of at least 8 carbon atoms. The term "phosphinylidene

group" is to be construed throughout the present specification as meaning a $\equiv P \rightarrow O$ group, (cf. J.C.S. 1952, page 5125).

The alkenyl substituted phosphorus compounds containing a phosphinylidene group may be derived from phosphoric acid, phosphonic acid, phosphinic acid or phosphine oxide. Thus a very suitable class of phosphorus compounds is that having the general formula:



where R_1 , R_2 and R_3 are alkenyl or cycloalkenyl radicals, a hydrogen atom, or an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical. At least one of R_1 , R_2 and R_3 is alkenyl or cycloalkenyl. The alkenyl radical may be α : β -mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably are β : γ mono-olefinically unsaturated hydrocarbon radicals of the formula $—CR^1—CR^1=CR^1$, where R^1 is a hydrogen atom or an alkyl

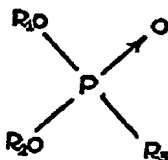
group preferably having no more than 6 carbon atoms. The alkenyl radicals may be the same or different, but are preferably the same, if a di- or trialkenyl derivative is desired, and more preferably they are allyl radicals. Alkenyl esters of phosphoric acid may be prepared by any method well-known in the art. For example the vinyl type esters may be prepared by dehydrohalogenation of compounds of the formula



where X is halogen, which compounds may be themselves prepared by reacting phosphorus/halogen compounds with ethylene oxide.

The allyl type esters can be prepared by reacting the desired phosphorus/halogen compound with a $\beta:\gamma$ mono-olefinically unsaturated alcohol in the presence of an acid-sequestrant, e.g. pyridine. Examples of suitable phosphoric acid esters are allyl dihydrogen phosphate, dibutyl allyl phosphate, diallyl hydrogen phosphate, diallyl methyl phosphate, diallyl phenyl phosphate, diallyl cyclohexyl phosphate, allyl methallyl hydrogen phosphate, divinyl hydrogen phosphate, divinyl phenyl phosphate, bis(2-ethylallyl) hydrogen phosphate, dimethallyl benzyl phosphate, dicrotyl hydrogen phosphate, bis(2-pentenyl) hydrogen phosphate, bis(2-hexenyl) isopropyl phosphate and triallyl phosphate.

A further class of phosphorus compounds useful as monomers in the present invention is that having the general formula:

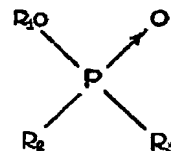


where at least one of the groups R_1 , R_2 and R_3 are alkenyl or cycloalkenyl groups and the other group(s) is (are) hydrogen, alkyl, cycloalkyl, aryl, alkaryl, or aralkyl. Preferably R_3 at least should be an alkenyl or cycloalkenyl radical. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α or β -alkyl substituted vinyl radicals, but preferably the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CR^1_2-CR^1=CR^1_3$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different but are preferably the same, if a di- or trialkenyl derivative is desired, more preferably they are allyl radicals. The above alkenyl derivatives of phosphonic acid may be prepared by any of the methods well-known in the art. For example, if R_1 and R_2 are both alkenyl

radicals, the dialkenyl phosphonates may be conveniently prepared by reacting the desired phosphonic dihalide with the desired mono-olefinically unsaturated alcohol in the presence of an acid-sequestrant, e.g. pyridine to produce the diester. When R_2 and R_3 are dialkenyl radicals, the desired compounds may be prepared by an Arbuzov reaction on a dialkyl alkenyl phosphite with an alkenyl halide. Where R_3 is the only alkenyl radical present, the required compound may be prepared by reacting phosphorus trichloride with an alkanol to produce a trialkyl phosphite which may then be reacted with an alkenyl halide to produce the required mono-alkenyl derivative.

Examples of suitable alkenyl derivatives of phosphonic acid are diethyl allylphosphonate, allyl butyl hydrogenphosphonate, allyl phenylphosphonic acid, diallyl phenylphosphonate, diallyl butylphosphonate, divinyl ethylphosphonate, the mono-allyl ester of allylphosphonic acid, allyl methallyl phenylphosphonate, dicrotyl hydrogenphosphonate, diallyl benzylphosphonate, divinyl phenylphosphonate, di(2-pentenyl) ethylphosphonate, and diallyl allylphosphonate.

A further class of alkenyl phosphorus monomers that may be used in forming the copolymers of the present invention is that having the general formula



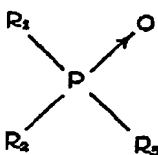
where at least one of the groups R_1 , R_2 and R_3 are alkenyl or cycloalkenyl and the other group(s) is (are) hydrogen, alkyl, cycloalkyl, aryl, aralkyl or alkaryl. Preferably R_1 at least is an alkenyl or cycloalkenyl radical. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α or β -alkyl substituted vinyl radicals, but preferably the alkenyl radicals are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CR^1_2-CR^1=CR^1_3$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different but are preferably the same where a di- or trialkenyl derivative is desired, more preferably they are allyl radicals. The above alkenyl derivatives of phosphonic acid may be readily prepared by any of the methods known in the art.

If R_1 is alkenyl the $\beta:\gamma$ mono-olefinically unsaturated derivatives may be prepared by direct esterification of a phosphonic acid with the desired $\beta:\gamma$ mono-olefinically unsaturated alcohol. Alternatively if R_1 is alkenyl and a dialkenyl derivative is desired having both

alkenyl radicals the same, a convenient method of preparation is to react a phosphonous dichloride with the desired $\beta:\gamma$ mono-olefinically unsaturated alcohol to form the diester of a phosphonous acid which undergoes an Arbuzov re-arrangement to form the ester of the corresponding phosphinic acid which may be separated from the reaction mixture by distillation.

If R_1 and R_2 are alkenyl radicals, the desired product may be obtained by reacting a dialkenyl phosphonous halide with a suitable alcohol or phenol in the presence of an acid sequestrant, e.g. dimethyl aniline. Examples of alkenyl derivatives of phosphinic acid are allyl phosphinate, the allyl ester of phenyl allyl phosphinic acid, the allyl ester of allyl phosphinic acid, the vinyl ester of vinyl-phenylphosphinic acid, diallyl phosphinic acid, allylmethylphosphinic acid, ethyl diallylphosphinate, phenyl divinylphosphinate, methyl allylmethylphosphinate and triallyl phosphinate.

A still further class of alkenyl phosphorus compounds useful in the present invention is that having the general formula:



where at least one of R_1 , R_2 and R_3 are alkenyl or cycloalkenyl radicals and the other group(s) is (are) hydrogen atom or an alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radical. The alkenyl radicals may be $\alpha:\beta$ mono-olefinically unsaturated hydrocarbon radicals, e.g. vinyl or α - or β -alkyl substituted vinyl radicals, but preferably R_1 and R_2 are $\beta:\gamma$ mono-olefinically unsaturated hydrocarbon radicals of the formula $-CR^1-CH=CH-R^2$, where R^1 is a hydrogen atom or an alkyl group preferably having up to six carbon atoms. The alkenyl radicals may be the same or different, but preferably they are the same if a di- or trialkenyl derivative is desired and more preferably they are allyl groups. Such phosphine oxides may readily be prepared by the reaction between a mono- or dihalophosphine or phosphorus trichloride and the desired alkenyl Grignard reagent followed by air oxidation. Alternately such compounds may be prepared by reacting a compound of the formula R_nRX_{3-n} , where R is aryl or alkyl or alkenyl and n is 1 or 2, with sulphur dioxide and chlorine to produce $R_nP(O)X_{3-n}$, and then reacting this product with an alkenyl reagent. Exemplary of suitable phosphine oxides are allyl butyl phenyl phosphine oxide, diallyl phenyl phosphine oxide, divinyl phenyl phosphineoxide, diallyl ethyl phosphine oxide,

diallyl benzyl phosphine oxide, allyl methallyl phenyl phosphine oxide, dimethallyl phenyl phosphine oxide, dimethallyl isopropyl phosphine oxide and triallyl phosphine oxide.

Mixtures of two or more of the foregoing monomers can be used if desired. Where it is desired to include the oleophilic hydrocarbon chain of at least 8 carbon atoms in the phosphorus containing monomer, this can readily be done for example by reacting a compound having the formula $(RO)(A)P(O)H$ where A may be aryl, alkyl, alkoxy, aroxy or hydrogen, and R is alkyl or aryl, with an olefin having at least 8 carbon atoms in the presence of a free radical initiator. The product can then be transesterified to replace the alkoxy or aroxy group(s) by alkenoxy group(s).

Typical of the other polymerisable mono-olefinically unsaturated compounds with which the foregoing phosphorous compounds may be copolymerised are acrylic acid and α -substituted acrylic acids and their derivatives, such as their esters, nitriles and amides. Examples of such compounds are acrylic acid, methacrylic acid, ethacrylic acid, α -phenyl acrylic acid, the alkyl esters thereof, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, octyl, nonyl, lauryl, cetyl, oleyl, stearyl and cyclohexyl esters, acrylamide, α -methacrylamide, α -ethacrylamides, laurylacrylamide, acrylonitrile, α -methacrylonitrile, α -ethacrylonitrile, α -propylacrylonitrile, 2-butyl 2-hexenenitrile, 2-propyl 2-pentene-nitrile, 2-chloroethyl 2-butenenitrile, 2-ethyl 3-chloro 2-butenenitrile, 2-isopropyl 3-bromo 2-pentenenitrile, and α -isopropyl β -cyclohexylacrylonitrile.

Other compounds which may be used to form the copolymers used in the present invention are vinyl esters of organic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl laurate, vinyl stearate and vinyl benzoate, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl phenyl ether, vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, and phenyl vinyl ketone, vinyl aryl compounds such as styrene, ortho-methyl styrene, para-methyl styrene, para-ethyl styrene, α -methyl styrene and other alkyl derivatives of styrene in which the alkyl group or groups may be substituted in the ring or in the side chain or both, vinyl naphthalene and vinyl diphenyl, vinyl halides, e.g. vinyl chloride and vinyl fluoride and vinylidene halides, e.g. vinylidene chloride and vinylidene fluorochloride. Allyl esters, ethers and ketones corresponding to the vinyl compounds listed above may also be used. Alpha, beta-unsaturated polycarboxylic acids and their derivatives such as maleic, fumaric, citraconic, itaconic and aconitic acids and their mono- and polyesters with aliphatic and aromatic alcohols,

and their amides and nitriles, may also be used.

Other compounds which may be used to form the phosphorus containing copolymers used in the present invention are the α -olefin particularly those having more than eight carbon atoms, amino-substituted olefins, e.g. p-(β -diethylaminoethyl)styrene and nitrogen-containing heterocyclic compounds having a mono-olefinically unsaturated substituent, e.g. the vinyl pyridines (whether 2-, 3- or 4-substituted) and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 3-methyl-5-vinyl pyridine, 4-methyl-2-vinyl pyridine, 4-ethyl-2-vinyl pyridine and 2-butyl-5-vinyl pyridine. Vinyl lactams are also suitable monomers, particularly the N-vinyl pyrrolidones or N-vinyl piperidones. The vinyl radical may be mono-alkyl substituted.

Of the above listed monomers copolymerisable with the phosphorus containing monomers according to the present invention, it is preferred that they contain an oleophilic hydrocarbon chain of at least eight carbon atoms which is preferably an alkyl radical of 12 to 20 carbon atoms. It will be appreciated that mixtures of the above monomers may be used in forming the copolymers used as lubricating oil additives according to the present invention. Particularly preferred copolymers are those formed from dialkenyl substituted phosphorus compounds with a higher alkyl ester of an acrylic or methacrylic acid, i.e. where the ester group contains 8 or more carbon atoms, e.g. lauryl methacrylate. Minor proportions of lower alkyl esters of acrylic or methacrylic acids, e.g. methyl methacrylate, may advantageously be present in such copolymers.

The molar ratio of phosphorus containing monomer to the polymerisable comonomer may vary between wide limits and generally lies between 20:1 and 1:20. Preferably the ratio lies between 5:1 and 1:10, with ratios between 3:1 to 1:5 being especially suitable.

The copolymers of the invention can be prepared by any suitable means. Normally the reactants are copolymerised in the presence of a catalyst. Oxygen-yielding catalysts, such as organic peroxides, may be used. These may be aliphatic, aromatic, heterocyclic, or alicyclic peroxides, such as diethyl peroxide, tertiary butyl hydroperoxide, di(tertiary butyl) peroxide, benzoyl peroxide, dimethyl thienyl peroxide, dilauroyl peroxide and urea peroxide. Other catalysts include sodium bisulphite, diethyl sulphoxide, ammonium persulphate, alkali metal perborates and azo compounds, e.g. azo-(bis-isobutyro) nitrile. The catalysts are generally used in an amount of 0.1 to 5% by weight of the reactants.

The copolymerisation reaction may be carried out under a variety of conditions. For example, the reaction can be carried out in

the presence or absence of an inert solvent, such as a hydrocarbon, under the blanket of nitrogen or carbon dioxide and at a temperature varying from room temperature or lower to about 180°C or higher for a period of from about 2 to 48 hours.

The following examples illustrate methods of producing copolymers of the present invention.

EXAMPLE I

A solution of 277 g. of allyl alcohol and 326 g. pyridine and 280 ml of ether was cooled to approximately -30°C by means of a bath of iso-propyl alcohol (I.P.A.)/Cardice (the word 'Cardice' is a registered trade mark) and was then added to a solution of 255 g. phosphorus oxychloride in 132 ml. ether over a period of two hours. After the first hour a further 100 ml. of ether was added to facilitate stirring. The reaction mixture was stirred for a further three hours after which time the pyridinium chloride formed was filtered off. The filtrate was evaporated leaving triallylphosphate as a clear yellow oil.

51 g. of the triallylphosphate was dissolved in 100 mls. of I.M.S. and refluxed with 100 mls of 5N aqueous solution hydroxide for two hours. The solvents were then removed under reduced pressure (100°C/15 mm) and the residual oil was extracted with ether in order to remove unhydrolysed phosphate. The oil was then treated with dilute hydrochloric acid until acid and the oil thus separated was extracted with ether to produce diallyl hydrogen phosphate.

A mixture of 3.4 g. of the diallyl hydrogen phosphate and 25 g. of lauryl methacrylate in 15.5 g. of technical white oil and 20 ml. of benzene was treated with 0.5 g. benzoyl peroxide and treated at 70°C. for 18 hours with stirring. The benzene was then evaporated to leave the copolymer as a viscous, oil-soluble product. The molar ratio of the diallyl hydrogen phosphate to lauryl methacrylate in the copolymer was 1:6.

EXAMPLE II

Phenylphosphonous dichloride was prepared by refluxing together 525 mls phosphorus trichloride, 468 mls benzene and 300 g. of aluminium chloride for four hours. Phosphorus oxychloride (223 mls) was then added and the mixture briefly refluxed. Excess benzene and phosphorus trichloride was evaporated under vacuum and the residue cooled to about 40°C and extracted with ligroin. From the extract, crude phenylphosphonous dichloride was recovered and purified by redistillation under reduced pressure.

A solution of 60.5 g. of allyl bromide in 285 ether was added dropwise to 12 g. magnesium in 100 mls ether. After stirring for 1 hour, 23 g. of phenylphosphonous dichloride in 100 mls of ether was added and the mixture stirred overnight. A solution of 50 g. of

ammonium chloride in 250 mls. water was added and the ethereal layer was separated, dried over sodium sulphate and evaporated.

The resultant crude diallylphenylphosphine was purified by redistillation. All these operations were conducted in a nitrogen atmosphere.

5.5 g. of the diallylphenyl phosphine was dissolved in 12 mls of benzene and air passed through the solution for thirty minutes to produce diallyl phenyl phosphine oxide. To this solution was added 23 ml. benzene, 15 g. of technical white oil, 7 g. of lauryl methacrylate and 0.5 g. of benzoylperoxide. The mixture was heated to 75°C. and stirred for 24 hours. At the end of each of the first three hours, a further amount of 7 g. lauryl methacrylate was added and with the third addition, a further 0.5 g. of benzoyl peroxide was added. The benzene was evaporated at reduced pressure and the residue heated at 100°C/1 mm Hg for 30 minutes. The resulting copolymer solution of diallyl phenyl phosphine oxide and lauryl methacrylate in technical white oil was soluble in mineral oil. The molecular ratio of diallyl phenyl phosphine oxide to lauryl methacrylate was 1:4.

EXAMPLE III

Phenyl phosphonous dichloride (prepared as in Example II, 90 g) was dissolved in carbon tetrachloride (500 ml) and the whole cooled to -50°C by a cardice/IPA coolant. Dry chlorine gas was now bubbled into the solution until the exothermic reaction was complete. The product was filtered whilst cool to give a residue of phenyl phosphonic tetrachloride. Further quantities of this material was obtained by evaporation of the mother liquors. The product was purified by recrystallisation from carbon tetrachloride, followed by drying in a vacuum desiccator.

Phenyl phosphonic tetrachloride (63 g) was dissolved in benzene (250 ml) and the stirred mixture treated with sulphur dioxide until reaction was complete. The reaction is rapid and the phenyl phosphonic dichloride Ph. POCl_2 produced was recovered by distillation b.p. 87°C/1 mm. Hg. Phenyl phosphonic dichloride (49 g) was added slowly with stirring to a solution of allyl alcohol (29 g) and pyridine (40 g) in ether (250 ml) cooled to 0°C. The rate of addition was such that the temperature of the mixture remained at 0°C. Stirring was continued for 2 hours after complete addition. The reaction product was filtered to remove pyridine hydrochloride and the residue washed with 200 ml. ether. The ether was evaporated from the filtrate and the residue distilled to give diallyl phenyl phosphonate b.p. 112°C/0.3 mm Hg.

To the solution of diallyl phenyl phosphonate (5.9 g.) and lauryl methacrylate (25.4 g.) in mineral oil (15.5 g) at 140°C, di-tert-butyl peroxide (0.4 ml) was added and the whole stirred vigorously. The solution

was maintained under these conditions for 5 hours. The product had a molar ratio of 1:4 diallyl phenyl phosphonate to lauryl methacrylate and was a 66.7% concentrate in mineral oil. This concentrate was readily soluble in further samples of mineral oil.

EXAMPLE IV

To a solution of allyl alcohol (135 g) and pyridine (168 g) in diethyl ether (2000 ml), phenyl phosphonous dichloride was added slowly with stirring. The rate of addition was adjusted to maintain a gentle reflux. Stirring and refluxing were continued for a further two hours after complete addition. Pyridine hydrochloride was filtered off and the residue washed with more ether (500 ml). The ether was evaporated from the filtrate and the product distilled, the bulk of the material (allyl phenyl allylphosphinate) boiling at 102°C/0.4 mms. Hg. Small amounts of diallyl phenylphosphonite are separated during the distillation b.p. 79°C/0.4 mms. Hg.

To a solution of allyl phenyl allylphosphinate (6 g) and lauryl methacrylate (28 g) in mineral oil (68 g) at 140-5°C di-tert-butyl peroxide (0.4 ml) was added and the whole stirred vigorously for 24 hours. The product was heated at 100°C/0.5 mm. Hg. for 30 minutes but no distillate was obtained. This product had a 1:4 molar ratio of allyl phenyl allylphosphinate to lauryl methacrylate and was a 33.3% concentrate in mineral oil.

EXAMPLE V

151.2 gm of phosphorus trichloride was added to a solution of 151.8 gm of ethanol and 269 gm of pyridine in 151.8 gm of a petroleum ether boiling at 60-80°C, over a period of two hours. The temperature was maintained at 0-5°C by a cardice/IPA cooling bath. The reaction mixture was stirred for a further hour after complete addition, during this time the mixture was allowed to warm to room temperature. The product was filtered to remove pyridine hydrochloride and the solvent and phosphorus trichloride were then stripped from the filtrate. The residue was distilled to give triethyl phosphite.

121 gm of allyl bromide containing a small quantity of hydroquinone was refluxed in a 500 ml. flask under a 10 inch column packed with glass beads, 140 gms of triethylphosphite was added starting at a rate which maintained a steady reflux. Material boiling at 37-39°C was run off from a Weir head at the top of the column. After 8 hours, no more low boiling material remained and the reaction mixture was distilled to produce diethyl allylphosphonate.

133.5 gms of diethyl allylphosphonate, 190.5 gms lauryl methacrylate, 445 gms of a SAE 10W30 grade mineral oil and 7.5 gms of di-tert-butyl peroxide were mixed and stirred together at 145°C. After $\frac{1}{2}$ hour a further quantity of 190.5 gms laurylmethacrylate was added, this was repeated after 2 hours and

again after 4 hours. The product was then stirred for a further 90 minutes. The mixture was then stripped at 140°C and 0.15 mm Hg pressure and a residue consisting of a 66.6% concentrate of a copolymer of diethyl allyl-phosphonate and lauryl methacrylate in a molar ratio of 1:8 in the mineral oil was recovered.

EXAMPLE VI

557 gms of allyl alcohol, 724 gms of pyridine and 500 mls of sodium dried toluene were stirred at 0–5°C. 413 gms of phosphorus trichloride in 100 mls of sodium dried toluene was then added whilst maintaining the temperature of 0–5°C. The product was stirred for ½ hour and then the amine hydrochloride was filtered off. The toluene was then stripped off leaving triallyl phosphite.

448 gms of n-butyl bromide containing a small amount of hydroquinone was heated to reflux in a vessel fitted with a column packed with glass beads surmounted by a Weir head. 220 gms of triallyl phosphite was added and refluxing continued for 20 hours and material boiling below 97°C was removed. Excess butyl bromide was then distilled off and the residue comprised diallyl butylphosphonate. 109 gms of diallyl butylphosphonate, 508 gms of lauryl methacrylate, 927 gms of an SAE 10W30 grade mineral oil and 7.6 gms of di-tert. butyl peroxide were reacted at 145°C for 4 hours. The final product was 40% wt. concentrate in the oil of a copolymer of diallyl butylphosphonate and lauryl methacrylate having a monomer ratio of 1:4.

Other copolymers of this invention include those listed below.

Diallyl cyclohexylphosphate/vinyl laurate, dimethallyl hydrogen phosphate/lauryl methacrylate, diallyl phenyl phosphonate/vinyl laurate, dimethallyl ethylphosphonate/oleyl maleate, allyl allylphosphinate/lauryl methacrylate, diallyl phosphinic acid/stearyl methacrylate, and diallyl ethylphosphine oxide/lauryl methacrylate.

The lubricating oil to which the copolymers may be added to provide lubricating compositions of the invention can be any natural or synthetic oil having lubricating properties. Thus, the oil can be a hydrocarbon lubricating oil obtained from paraffinic

or naphthenic crude or mixtures thereof. The viscosity of these oils may vary over a wide range, such as from 100 SUS at 100°F to 100 SUS at 210°F. The hydrocarbon lubricating oil may be blended with fatty oils such as castor oil or lard oil, and/or with synthetic lubricating oils such as polymerised olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e.g. di(2-ethyl hexyl)sebacate, dioctyl phthalate and trioctyl phosphate and polyalkyl silicone polymers such as dimethyl silicone polymers. If desired, the synthetic lubricating oils may be used as the sole base lubricating oil or admixed with fatty oils or derivatives thereof.

In the lubricating compositions of the present invention the polymeric additive is present in a minor proportion by weight based on the total composition, generally from 0.01% to 20% and preferably from 0.1% to 8% by weight.

It will be understood that the lubricating compositions of the invention may be modified by the addition thereto of minor proportions of other additives such as methacrylate polymers, metal dithiophosphates, e.g. zinc di-2-ethylhexyl dithiophosphate, metal organic sulphonates, e.g. neutral or basic calcium, barium or zinc petroleum sulphonate; metal thiocarbamates, e.g. zinc, chromium or calcium dibutyl or diamyl dithiocarbamate; amines, e.g. phenyl-alpha-naphthylamine or octadecylamine; alkylated phenols and alkylated bisphenols, e.g. 2,6-ditertiarybutyl-4-methylphenol and 4,4'-methylene bis(2,6-ditertiarybutyl phenol); organic sulphides, e.g. dibenzyl disulphide.

Lubricating compositions of the present invention are useful as engine oil, gear oils, turbine oils and various other fields of lubrication where good detergency, viscosity temperature characteristics and load carrying properties are essential.

Compositions of this invention are illustrated by the following formulations; the ratios in brackets being the mole ratios of the monomers used for preparing the copolymers. The mineral lubricating oil used is an oil having a viscosity of 10 cs at 210°F.

COMPOSITION A

Copolymer of diallyl hydrogen phosphate/lauryl methacrylate (1 : 6)	4% wt.
Mineral oil	balance

COMPOSITION B

Copolymer of diallyl hydrogen phosphate/lauryl methacrylate (1 : 8)	4% wt.
Mineral oil	balance

COMPOSITION C

Copolymer of diallyl phenyl phosphine/oxide lauryl methacrylate (1 : 4)	3.5% wt.
Mineral oil	balance

COMPOSITION D

Copolymer of the allyl ester of phenyl-prop-2-enyl phosphinic acid/lauryl methacrylate (1 : 4)	2.0% wt.
4,4'-methylene-bis(2,6-di-tert. butyl phenol)	0.75% wt.
Mineral oil	balance

COMPOSITION E

Copolymer diallyl phenyl phosphonate/lauryl methacrylate (1 : 4)	6.8% wt.
Mineral oil	balance

COMPOSITION F

Copolymer of diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	3.9% wt.
4,4'-methylene-bis(2,6-ditertiarybutyl phenol)	0.75% wt.
Mineral oil	balance

COMPOSITION G

Copolymer of diethyl allyl phosphonate/lauryl methacrylate (1 : 8)	2% wt.
4,4'-methylene-bis(2,6-ditert. butyl phenol)	0.75% wt.
Mineral oil	balance

COMPOSITION H

Copolymer of diallyl butylphosphonate/lauryl methacrylate (1 : 4)	2% wt.
4,4'-methylene-bis(2,6-ditert. butyl phenol)	0.75% wt.
Mineral oil	balance

In order to illustrate the properties of lubricating compositions according to the present invention, certain compositions were subjected to tests in the following manner.

The thickening ability of the copolymers used as additives in the present invention was assessed in terms of the VT coefficient, calculated from the formula:

$$VT = \frac{\frac{\eta_{\text{blend}}^{210^\circ \text{ F.}}}{\eta_{\text{base oil}}^{210^\circ \text{ F.}}} - \frac{\eta_{\text{blend}}^{100^\circ \text{ F.}}}{\eta_{\text{base oil}}^{100^\circ \text{ F.}}}}{\frac{\eta_{\text{blend}}^{210^\circ \text{ F.}}}{\eta_{\text{base oil}}^{210^\circ \text{ F.}}} - \frac{\eta_{\text{blend}}^{100^\circ \text{ F.}}}{\eta_{\text{base oil}}^{100^\circ \text{ F.}}}} \times 100$$

where η is the viscosity.

Various copolymers were added to a base mineral lubricating oil having a viscosity of 10 cs at 210°F and the VT values deter-

mined from the above equation. The results are contained in Table I. 5

TABLE I

Copolymer	Concentration	VT
Diallyl hydrogen phosphate/lauryl methacrylate (1 : 6)	4% wt.	109
Allyl ester of phenyl allyl phosphinic acid/lauryl methacrylate (1 : 4)	4.1% wt.	117
Diallyl phenyl phosphine oxide/lauryl methacrylate (1 : 4)	2% wt.	109

10 These figures represent good thickening properties. The dispersant properties of various compositions were illustrated in the following manner.

15 1 part by weight of used straight mineral oil containing about 2% w of oil-insolubles from a diesel engine was mixed with 5 parts of the unused mineral oil of Compositions A—H. In this blend the insoluble particles

are clustered. Other blends are made containing, as before, 1/6th of used oil, and the remaining 5/6th a series of increasing concentrations of one of the additives in the unused mineral oil. At a particular concentration the insoluble particles become dispersed, and this concentration is taken as a measure of the discrepancy of the additive. Some results are given in Table II. 25

TABLE II

Copolymer	Concn. of copolymer required to disperse clusters in mg per g blend
Diallyl phosphate/lauryl methacrylate (1 : 6)	0.4
Diallylphenylphosphine oxide/lauryl methacrylate (1 : 4)	0.3
Diethyl allylphosphonate/lauryl methacrylate (1 : 4)	0.8
Triallyl phosphate/lauryl methacrylate (1 : 4)	1.7
Diethyl allylphosphonate/lauryl methacrylate (1 : 8)	0.67
Diallyl phenylphosphonate/lauryl methacrylate (1 : 4)	1.0
A mixture of diallyl butylphosphonate and diallyl phosphate of 9 : 1 molar ratio/lauryl methacrylate (1 : 4)	0.67
A mixture of diallyl butylphosphonate and diallyl phosphate in 4 : 1 molar ratio/lauryl methacrylate (1 : 4)	0.67

5 Compositions D, F, G and H exhibited
good low temperature performance properties
when used in an automotive engine as is
evidenced by absence of sludge deposition in
the sump. Further, Compositions F and H
were submitted to an anti-scuffing test in an
automotive engine in which the cam wear
and degree of tappet scuffing is indicative of
10 the load carrying capacity of the oil. Com-
pared with a similar formulation, but in which
the 3.9% of the copolymer according to the
invention is replaced by 4% wt. of a copoly-
mer of laurylmethacrylate and vinyl pyrrol-

idone, Composition F exhibits a 60% reduction in cam wear and Composition H exhibits
a 50% reduction in the amount of tappet
scuffing and a 90% reduction in cam wear.
Also, compositions A and D, when subjected
to a test for extreme pressure properties on the
4-ball machine, exhibited 2½ second seizure
20 delay loads of 137 kg and 92 kg respectively
compared with 65 kg for the base oil.

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